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SURFACE CHARACTERIZATION THROUGH SHAPE OSCILLATIONS OF DROPS IN MICROGRAVITY AND 1-g

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ABSTRACT

The goal of these experiments is to determine the rheological properties of liquid drops of single or multiple components in the presence or absence of surface active materials by exciting drops into their quadrupole resonance and observing their free decay. The resulting data coupled with appropriate theory should give a better description of the physics of the underlying phenomena, providing a better foundation than earlier empirical results could.

The space environment makes an idealized geometry available (spherical drops) so that theory and experiment can be properly compared, and allows a "clean" environment, by which is meant an environment in which no solid surfaces come in contact with the drops during the test period. Moreover, by considering the oscillations of intentionally deformed drops in microgravity, a baseline is established for interpreting surface characterization experiments done on the ground by ours and other groups.

Experiments performed on the United States Microgravity Laboratory (USML-1) demonstrated that shape oscillation experiments could be performed over a wide parameter range, and with a variety of surfactant materials. Results, however, were compromised by an unexpected, slow drop tumbling, some problems with droplet injection, and the presence of bubbles in the drop samples. Nevertheless, initial data suggests that the space environment will be useful in providing base-line data that can serve to validate theory and permit quantitative materials characterization at 1-g.

INTRODUCTION

A. Research Objectives

The primary goal of this research is to investigate the rheological properties of surfactant-bearing liquid drops. By comparing experimental results in the ideal environment of Spacelab to our theory for perfect spherical-equilibrium drops, the model can be validated. A generic theory which can handle arbitrary acoustic fields and static deformations can then be synthesized in order to have a technique for

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studying static and dynamic surface properties for surfactant-bearing drops which can be successfully applied in 1g experiments.

B. Background and Motivation

Consideration of the fluid mechanical oscillations of a pure liquid drop yields unique and well known values for the frequency and damping of single (in the present case, quadrupole) mode shape oscillations about a spherical equilibrium. However, the viscoelastic properties of even dilute surface concentrations of surfactant material affect the motion of the interface, thus coupling the two problems. The decrease in interfacial tension will shift the frequency downwards. Convective transport of the surfactant during oscillations will redistribute the surface concentration of surfactant, resulting in surface tension gradients. If this is not quickly compensated for by diffusive/sorptive transport from the bulk, then the resulting surface stress will give rise to a retarding flow, increasing the effective damping of the mechanical oscillations of the drop. These effects are controlled both by the type and concentration of surfactant, and the relative time scales of the processes involved: diffusion, sorption, and oscillation. Quantifying these changes by inferring interfacial shear and dilatational viscosities from the measurements and theory will allow prediction of the effects of small concentrations of surfactants.

Microgravity affords a unique combination of advantages which facilitate the comparison with existing theory and the development of a testable theory for the 1g case. Drops with an arbitrary equilibrium shape can be produced. This is so because the weight of the drop need not be supported by the external acoustic field. For comparison with the "ideal" theory, low-amplitude, spatially symmetric acoustic fields can be used to observe oscillations of a drop in air about a spherical equilibrium. Nonlinear acoustic effects (which cause distortion and rotation in 1g) are eliminated. Finally, the static deformation (always present in 1g experiments) can be continuously varied, allowing for the validation of models for the pressure/deformation interaction. The eventual coupling of this model with the validated model for surfactant transport in spherical drops will allow for the isolation of the effects of surfactants from the fluid/mechanical effects on the drop dynamics. This will allow researchers to perform relatively inexpensive 1g experiments for surfactant rheology determination, since the microgravity-confirmed model will correct for the fluid-mechanical effects present in high acoustic fields in 1g.

I. THEORY REVIEW

A. Surfactant-bearing drop oscillations

Equations based on the work of Lu et al.[1] have been developed which relate the surface properties (elasticity, surface viscosities, surface concentrations) to the frequency and damping of free quadrupole-mode oscillations for water drops in air with surfactant dissolved in the drops. The equations for diffusive transport in the bulk plus the equations for sorptive transport from the surface sublayer to the surface are coupled to the velocity field of the oscillation drop to provide a dynamic description of the problem. "Exact" numerical solutions and approximate analytic solutions are restricted to oscillations about a spherical equilibrium. The analytic results[2] can be described by the following equations, which assume that the sorption time scale << diffusion time scale << oscillation period, and that drops are large (>0.1mm) and viscosities small, comparable to water. [Other limiting cases of transport have been derived but are not included here.]

Transcendental equation for the droplet quadrupole shape oscillation:

The droplet shape is a function of time as $e^{-\alpha\omega t}$

where ω is the Lamb Frequency

α is the nondimensional coefficient

The transcendental equation for the droplet quadrupole shape oscillation is:

$$(\alpha x)^2 + P - 12\beta_S + \left(\frac{x}{\alpha}\right)^2 + Q(\alpha x)\left[\frac{16}{\alpha^2\chi^2}P\beta_S - \left(1+\alpha^{-4}\right)\left(3P - 4\beta_S\right)\right] = 0$$

where γ: surface tension

ρ, R, μ: droplet density, radius and (bulk) shear viscosity

β_D, β_S: surface dilatational and shear viscosity numbers

$\beta = -\partial\gamma/\partial \ln(\Gamma^*)$ surface dilatational elasticity

Γ^*,C^* surfactant surface and bulk concentrations

$$P = \frac{\beta\chi^2}{4G} + 2\beta_D$$

$$G = \alpha^2 - \frac{6}{y^2} + \frac{R\kappa C^*_{eq}}{z^2\Gamma^*_{eq}}\left\{\frac{\kappa_1}{2 - Q(\alpha z)} - \frac{C^*_{eq}D}{\Gamma^*_{eq}R}\right\}^{-1} \tag{1}$$

$\chi^2 = \rho R^2\omega/\mu$, $y^2 = \omega R^2/D_S$, $z^2 = \omega R^2/D$

D, D_S surfactant bulk and surface diffusion coefficients

κ, κ_1 surfactant surface and absorption and desorption coefficients

$$Q(\alpha\chi) = \alpha\chi\frac{j_{l+1}(\alpha\chi)}{j_l(\alpha\chi)}, \qquad j_l(\alpha\chi) \text{ is Bessel function}$$

Approximate solution:

Assuming

$\alpha^2 = i(1+\varepsilon)$

$\varepsilon = 0.0 \sim 0.1$, $\beta = 0.0 \sim 1$, $\beta_d = 0.0 \sim 10$, $\beta_s \sim 0$

For diffusion controlled surface transfer

$G = 1 - jR^{3/4}/\lambda$

where $i = \sqrt{-1}$, $j = \sqrt{i}$

$\lambda^2 = 8\gamma(\partial\Gamma^*/\partial C^*)^2/D$

then
$$\varepsilon = \frac{\dfrac{\beta\chi^2}{4G} - 10i - 2\beta_d i + 4\left[\dfrac{\beta}{G} + \dfrac{32(1-\beta_d)}{\chi^2}\right](\chi j - 5i)}{2\chi^2 - \left[4(1-3\beta_d) - \dfrac{3\chi^2\beta}{2G}i\right](\chi j - 5i)} \tag{2}$$

In the experiments, droplets with different surfactant concentrations are excited into quadrupole shape oscillations. By measuring their resonance frequencies and free damping constants, ε can be determined as a function of the droplet size. When fitting these experimental data with Eq.(2), we can estimate the droplet surface tension, surface elasticity and surface viscosity.

Note

1. Generally speaking, the surface shear viscosity is very small and is negligible.
2. The assumptions of the values of ε, β and β_d agree with the experimental results.
3. Langmuir equations, $n = \Gamma^*_{eq}/\Gamma^*_{\infty} = C^*_{eq}/(C^*_{eq}+a)$ and $\gamma-\gamma_0 = -\Gamma^*_{\infty}RT\ln(1-n)$, are used to express the relationships between the surface tension and the surfactant concentration. These equations, which are valid for the surfactant system at low concentrations, are widely used in the literature.

As an example of both exact and approximate solutions, Figure 1 shows the predictions for non-dimensional frequency and damping, plotted vs. surface dilatational elasticity. Similar agreement is found in plots vs. surface dilatational viscosity number. This theory is applied to ground-based experimental results presented in section 3 in order to infer surface properties. (This work will be reported in detail in an article to be submitted to the Journal of Colloid and Interface Science.)

B. Acoustic radiation pressure effects on drop deformation and location; Oscillation frequency shifts.

The importance of understanding the effects of the acoustic field on shape oscillations can be clarified with the aid of Figure 2. When a drop is spherical, the surface tension always serves to restore a deformed drop to its spherical shape. This is true, because work is done to increase the surface area from the spherical to non-spherical shape. But if a drop is deformed by an acoustic (or any other) field, then a change of this shape toward the more rounded shape actually requires negative work (because the surface area is getting smaller). The restoring force for this motion is not the surface tension, but rather the acoustic field. Therefore, if one oscillates drops about a deformed shape, one must understand in detail the role of any fields that exert a body force on the drop.

The acoustic scattering of a plane acoustic standing wave from a spheroidal drop has been treated theoretically, using the boundary integral technique. The assumptions of small deformations and spherical symmetry have been relaxed in this treatment, allowing the derivation of a self-consistent set of equations to be solved numerically for the unique combination of deformation and scattered acoustic field which solves the problem for known external pressure and drop properties (size, composition). This approach does not rely on small deformations and spherical harmonic expansions to derive the frequency of oscillations about such a deformed equilibrium shape as a function of the drop static deformation. The nonlinear coupling of the acoustic field to the drop during oscillation is explicitly accounted for in the description of the restoring force that returns a drop to its equilibrium state. Details of this procedure will be published by Shi.[3]

Two basic regimes of behavior are reviewed below.

B1. Small oscillations about a deformed shape

After specification of the velocity potential of zero on the surface, the drop position and shape are followed. Numerical damping is introduced until equilibrium is obtained. Then, the field conditions are perturbed in order to induce small oscillations about the deformed shape. Figure 3 shows an example in which a water drop with aspect ratio of 1.175 and ka = 0.4 (where k is the wave number and a is the spherical equilibrium radius) undergoes small oscillations. Both drop size and kinetic energy of the drop are shown as a function of time.

Plots of the results of the frequency of this oscillation vs. aspect ratio for a given ka are given in Section 3, when experimental results are reported. Two cases have been computed: the case of 0g and the case of 1g. By comparing these results with each other and with both ground-based and Spacelab experiments, one should be able to understand the role of the acoustic field in the oscillation dynamics and, therefore, be able to extract surface material properties from 1g experiments.

B2. Large-amplitude oscillations and unstable motions of drops

In this case the ultimate instability of an acoustically stressed drop is examined theoretically. Because the boundary integral method does not depend on small oscillations or spherical harmonic expansions, a completely general result can be obtained. For example, in the case of a water drop of 1.49 mm diameter and a frequency of 21.76 kHz (corresponding to ka = 0.3, which is similar to the ka

values of USML tests), it is found that at SPL of 167.2 dB the flattened drop becomes unstable and will break up, as shown in the sequence of Figure 4. These predictions are similar to experimental results reported by Lee et al.[4]

II. EXPERIMENTS

A. Ground-Based (1g)

Ground-based studies of shape deformation and oscillation inform microgravity work in two major ways: First, large numbers of carefully performed experiments with sophisticated diagnostic tools not possible in Spacelab provide invaluable experience in preparation for space-based work. Second, ground-based work will provide one test of new theoretical models for oscillations of a drop about a deformed shape. The ultimate test of the model will come in microgravity tests (as described in section 3.2)

An ultrasonic levitation cell operating at about 28 kHz has permitted a number of experiments with 1-3 mm diameter drops of water and aqueous solutions of surfactants. Experiments have included a) change in static deformation and position of drops as a function of the standing wave field strength (water drops only)[5] b) determination of free decay frequency and damping constant for water drops and for drops with varying surfactant type and concentration (drops typically have an aspect ratio of 1.1 for these tests)[see ref. 2] and c) frequency of maximum deformation for forced oscillation of drops (water drops only).

A1. Deformation vs. position in an acoustic field, and the determination of surface tension.

Figure 5 shows four frames of the same drop but at four different acoustic field strengths, and thus four different deformations and positions. The white dots around the photographic image represents the theoretical predictions. Tian et al.[6] have recently proposed a theory which allows one to predict the surface tension of an interface if one can measure the position change in the levitation field as a function of aspect ratio. For instance in Figure 6a there is a plot of the deformation and location of a water drop in an acoustic field of varying strength. In Figure 6b one finds the minimum deviation between theoretical predictions and the experiments of Fig 6a by adjusting the surface tension coefficient in the theory. In the particular example, it is seen that the minimum deviation occurs for a surface tension of 71 dynes/cm.

A2. Frequency of shape oscillations of deformed water drops

Figure 7 shows 1g experiments of free decay frequency versus aspect ratio for drops with *ka* ranging from 0.49 to 0.56, along with the theory of Shi who adapts the boundary integral method (as developed by Baker et al.[7] and Baker and Lundgren[8]) for the case of an acoustic field. Theoretical results are shown for drops of ka = 0.4 and 0.6. Frequency is normalized to the Lamb frequency (for quadrupole shape oscillations about a spherical shape). This agreement gives one confidence in the ability to apply this model to complex situations.

A3. Interfacial characterization of surfactant laden water drops

In Figure 8 measured free decay frequency and damping constant as a function of drop radius are shown for drops of three surfactant concentrations of N-octyl β D-glucopyranoside, a nonionic surfactant. (Concentrations are given as fractions of the CMC, critical micelle concentration). The process of extracting interfacial elasticity and viscosity is as follows: The curves are least-squares fitted, as shown by two examples in the figures for frequency and damping constant. Values of the interfacial parameters that are consistent with that fit and the theoretical model can then be plotted, as shown in Figures 9 and 10. Fits have also be performed for two other surfactants (Sodium Dodecyl Sulfate, SDS, an anionic surfactant, and Dodecyltrimethyl-ammonium bromide, a cationic surfactant). These results will be reported in reference 2.

B. Spacelab (USML-1) Results

Microgravity results allow one to extract materials properties from the data and accepted theory for small shape oscillations of spherical drops. Even more importantly, once one knows the properties from the microgravity experiments, one can then see if one can retrieve the same results using oscillations about a deformed shape and a modified but untested theoretical model for this case. If the model is successful, then the microgravity results will have informed the ground-based studies, and interfacial characterization based on oscillations of deformed drops can confidently continue in ground-based research.

The Drop Physics Module flown on USML-1 was designed for acoustical control and manipulation of drops. In order to obtain data from shape oscillations, both the X and Z views of the Module were recorded on video tape for all events, and for some oscillations a split screen X and Z view were filmed at speeds up to 120 frames per second. The quadrupole oscillation should appear in its classical oblate-prolate form in the X-view, and as a circle of increasing or decreasing size in the Z-view. However, in most sequences there was also a bothersome rotation (at about one rotation per second) about an arbitrary axis (often close to the Y-axis). Since the shape oscillations were of the order of 2-4 Hertz, the tumbling rotation represented a severe challenge in the data analysis.

In Figure 11 data from the X-view of a water drop of 2.0 cm diameter is fit with a decaying sinusoidal curve. From this fitted curve one obtains both frequency and damping constant.

In one USML-1 experiment a drop of 2.0 cm diameter was oscillated about several different deformed shapes. For an acoustic frequency of 1125 Hz, *ka* = 0.21. The cine record of these experiments in plotted in Figure 12, along with Shi's predictions for the case of 0g (and *ka* = 0.2, 0.4, and 0.6). The trend and absolute magnitudes appear to be in reasonable agreement with theoretical predictions for *ka* = 0.2, but the errors in the measurement and data analysis are too significant to have confidence in extracting interfacial properties.

CONCLUSIONS

Ground-based and microgravity experiments and new theoretical models both for the shape oscillations of drops in acoustic fields of arbitrary magnitude and for the transport behavior of surfactants in drops make possible both a more complete understanding of drop dynamics (including the conditions for instability) and the ability to extract surface properties from shape oscillations data.

Although initial microgravity data was compromised by instrument performance, the data that was obtained validated the overall approach for studying drop dynamics and measuring materials properties. Future work will be directed at solving instrumentation problems and continuing ground-based theoretical and experimental research in preparation for future microgravity tests.

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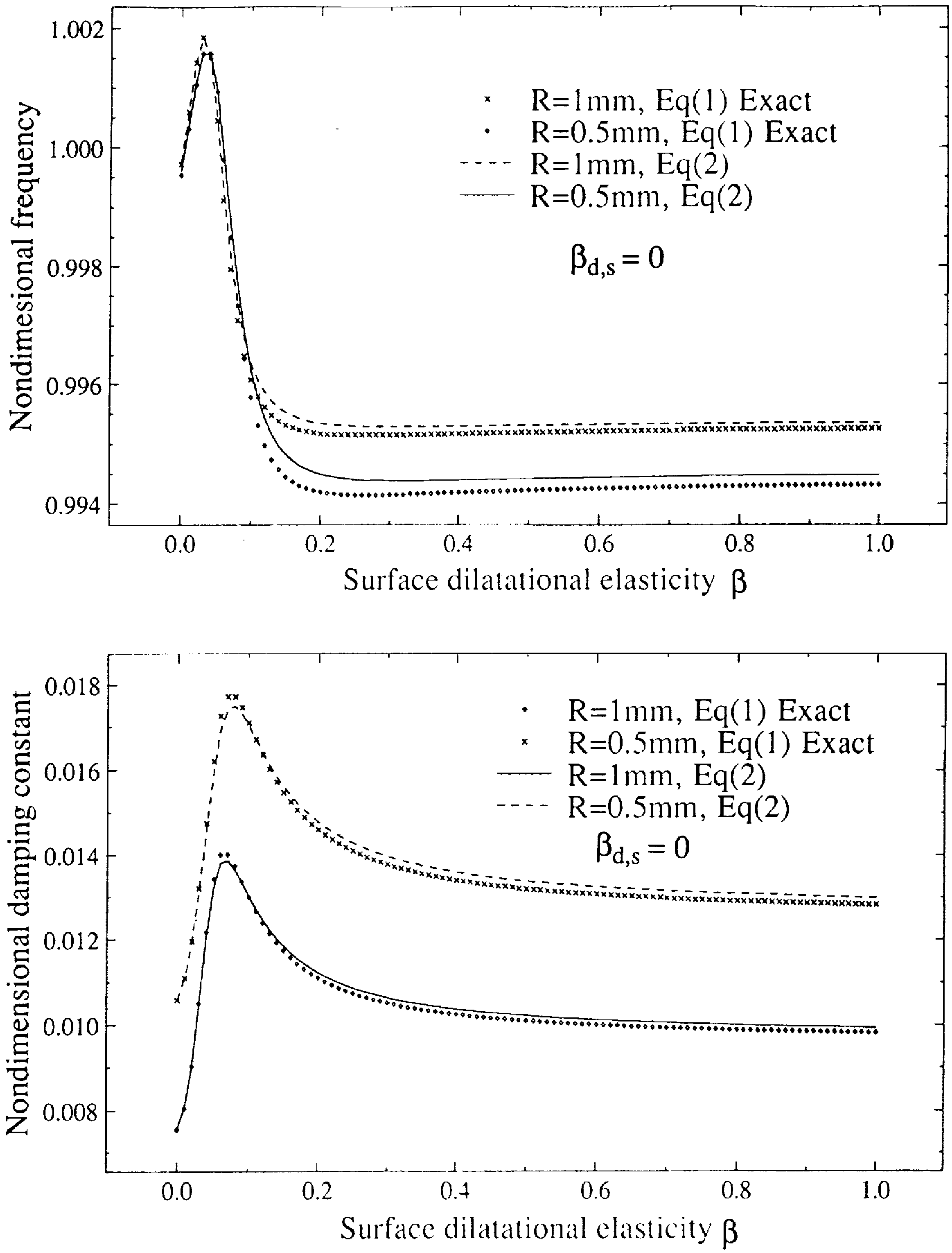
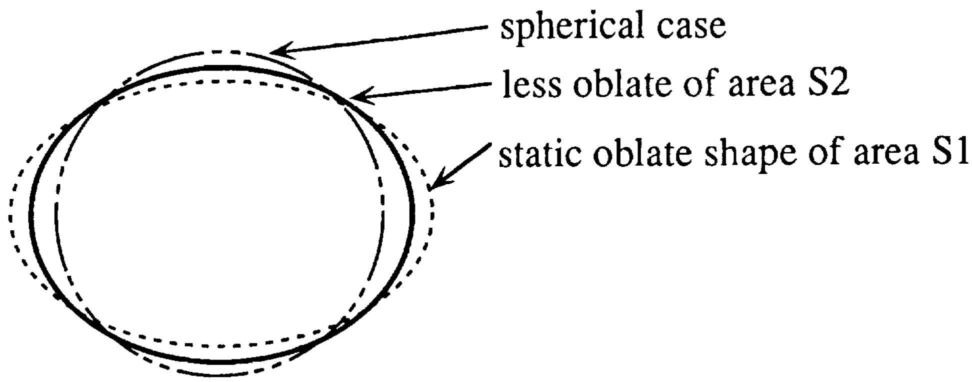


Figure 1a and b. Variations of the non-dimensional resonance frequency, Im (a), and the damping constant, Re (a), versus droplet surface dilatational elasticity. Here the surface dilatational and shear viscosities are zero.

Oscillations about deformed equilibrium

Effect on frequency



Drop		Restoring force
spherical equilibrium (low acoustic field)	$\rightarrow$	$\left.\begin{matrix}\text{prolate}\\ \text{oblate}\end{matrix}\right\} - \gamma$
oblate (S1) equilibrium (high acoustic field)		more prolate ($F_{rad} - \gamma$) more oblate ($\gamma - F_{rad}$)

$\therefore$ Oscillations nonlinearly coupled to acoustic field:

$$\boxed{E_p \cong \gamma \Delta S + W_{rad}}$$

Figure 2. Schematic showing shape oscillations about a deformed drop, and the relevant restoring forces.

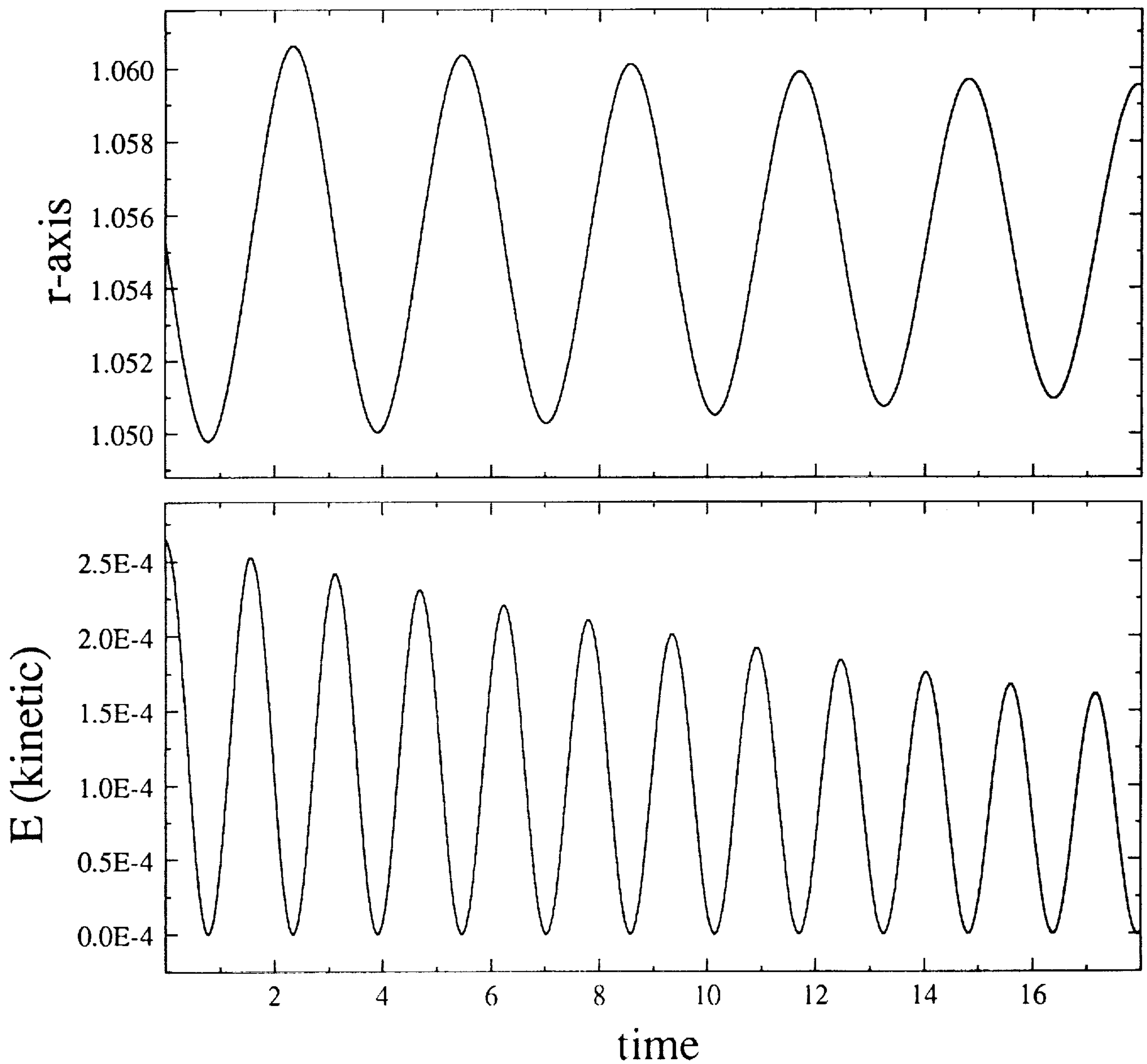


Figure 3. Predicted decay of acoustically deformed drop (aspect ratio 1.175; ka = 0.4) as seen through the r coordinate (lateral dimension) and the drop kinetic energy.

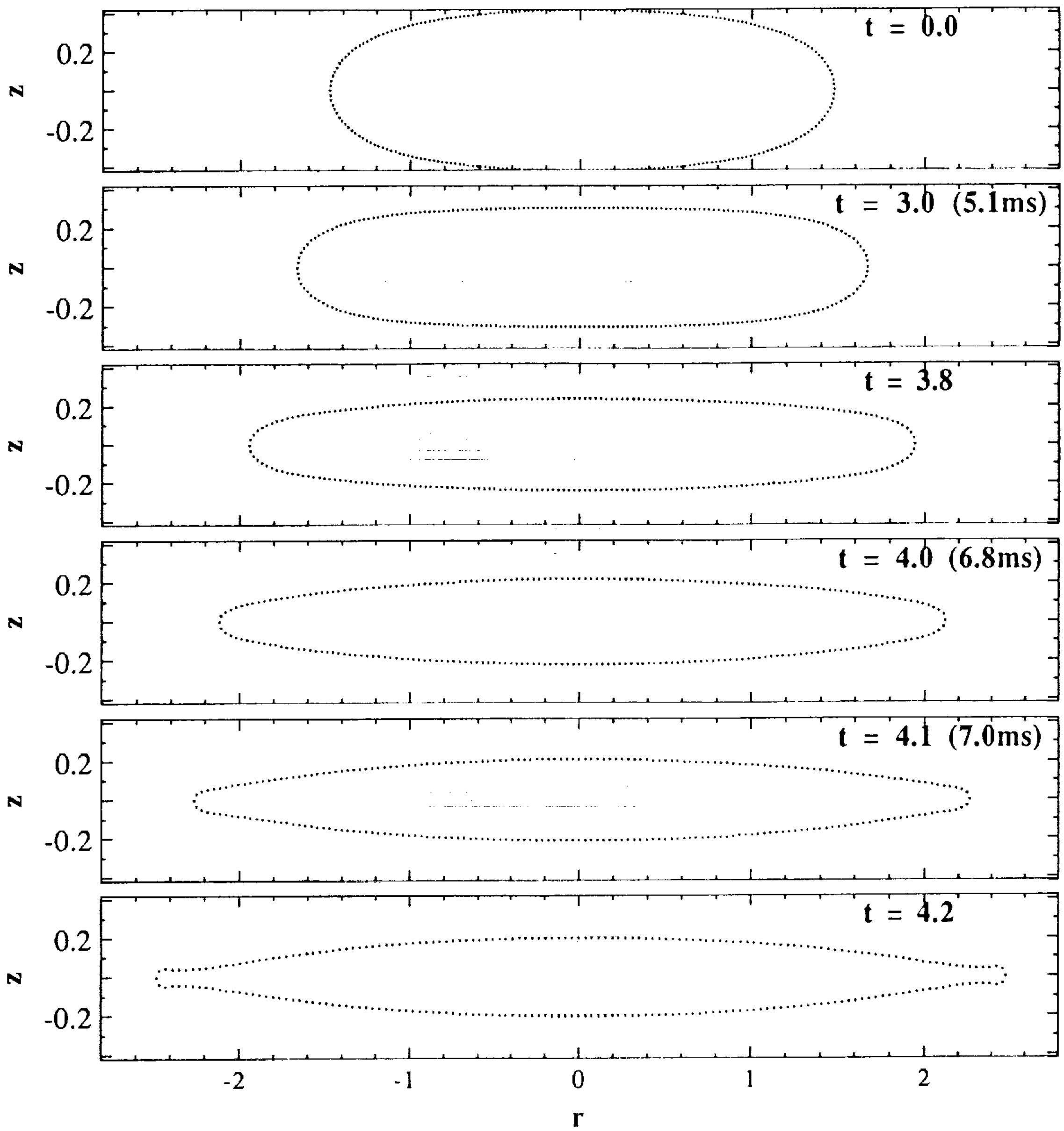


Figure 4 Sequence showing evolution of drop shape instability over a period of approximately 8 ms, for conditions described in text.

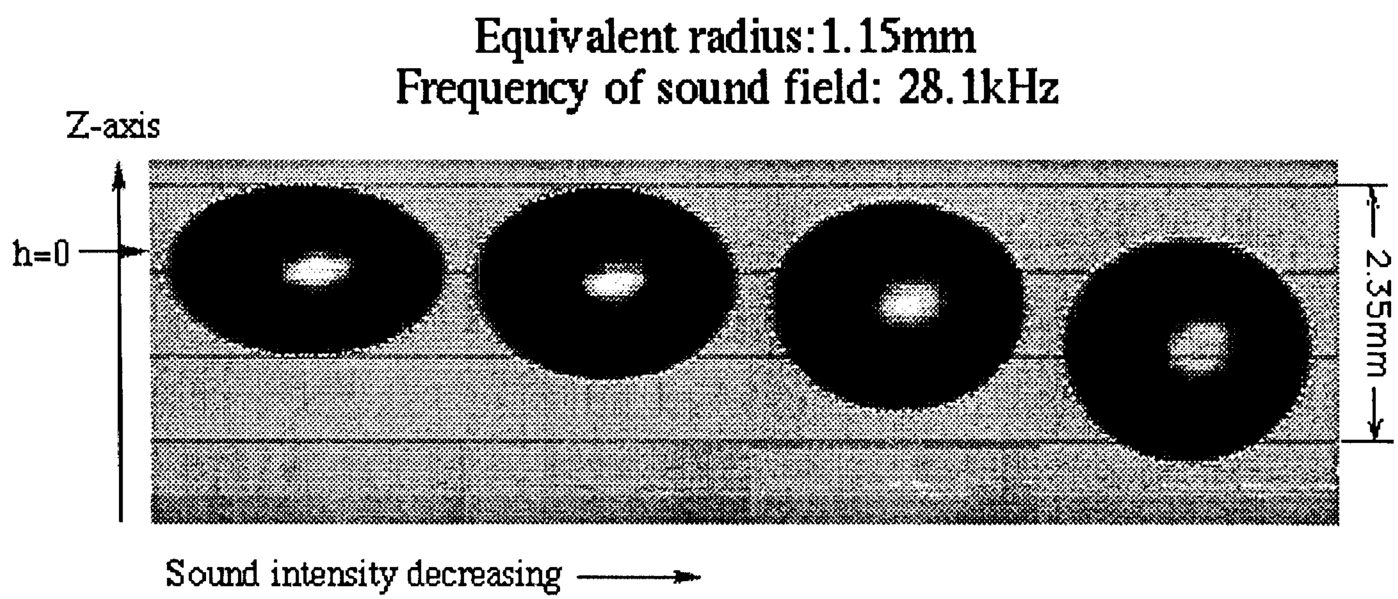
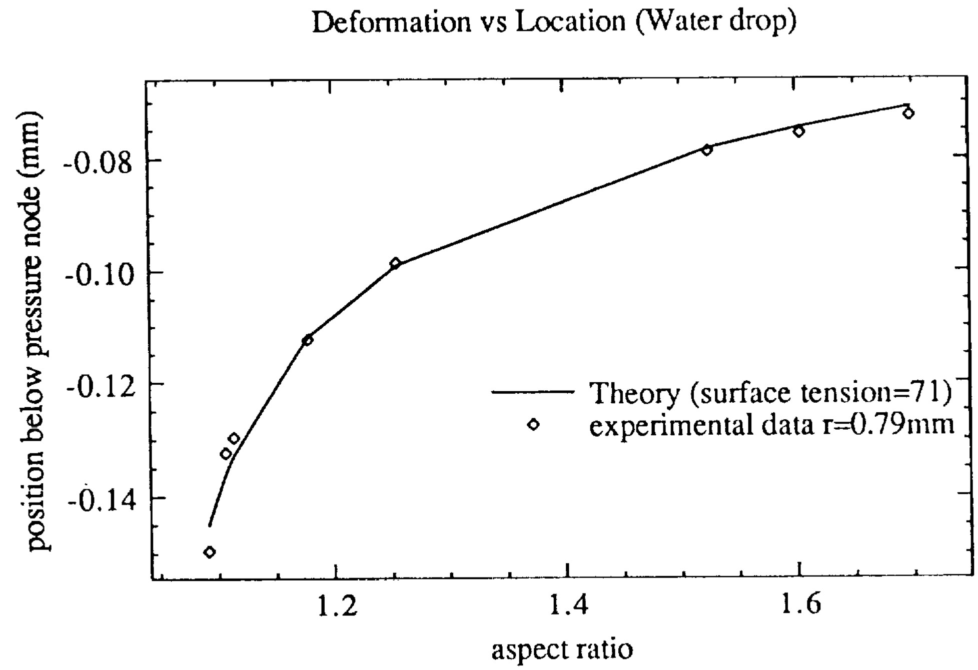


Figure 5 Experimental drop deformation and location, as affected by acoustic field. The white dots around the images are theoretical predictions. (From reference 5)



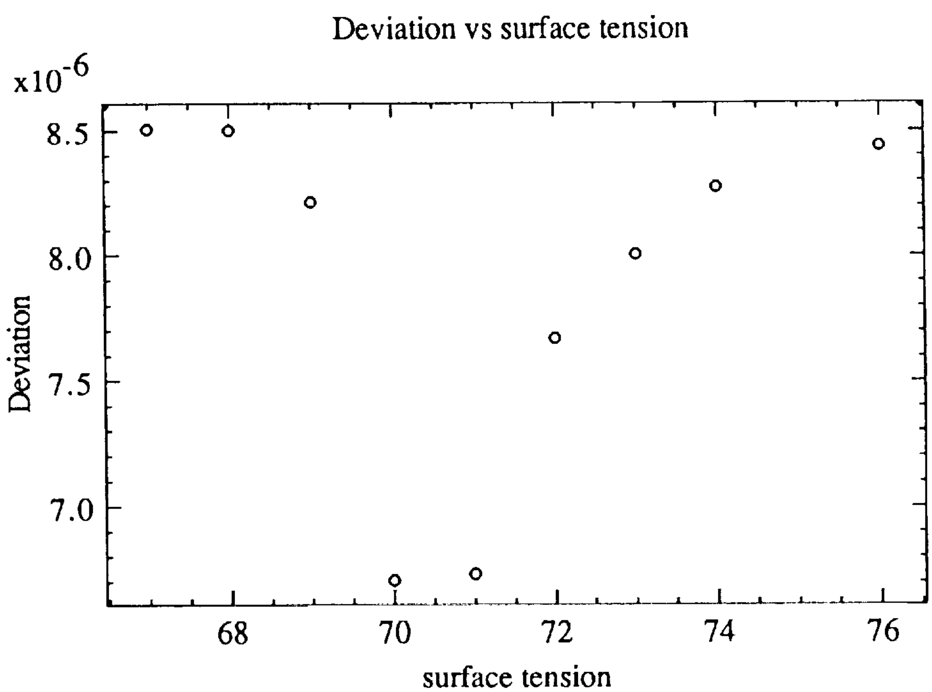


Figure 6a Experimental data of a water droplet deformations versus its locations. These data are fit with the theoretical model by using surface tension as a fitting parameter. (b) gives the standard deviation of these fittings. It shows that the best selection of the surface tension for this drop is about 71 dyn/cm.

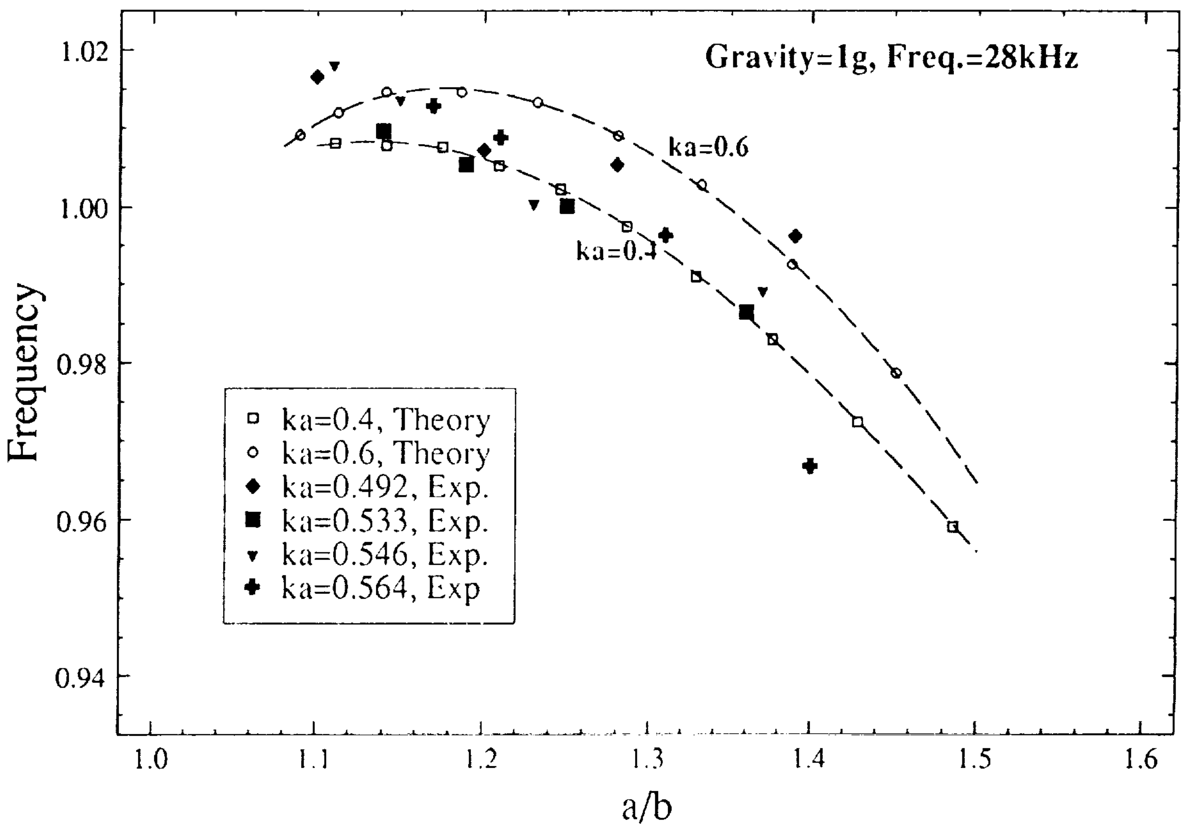
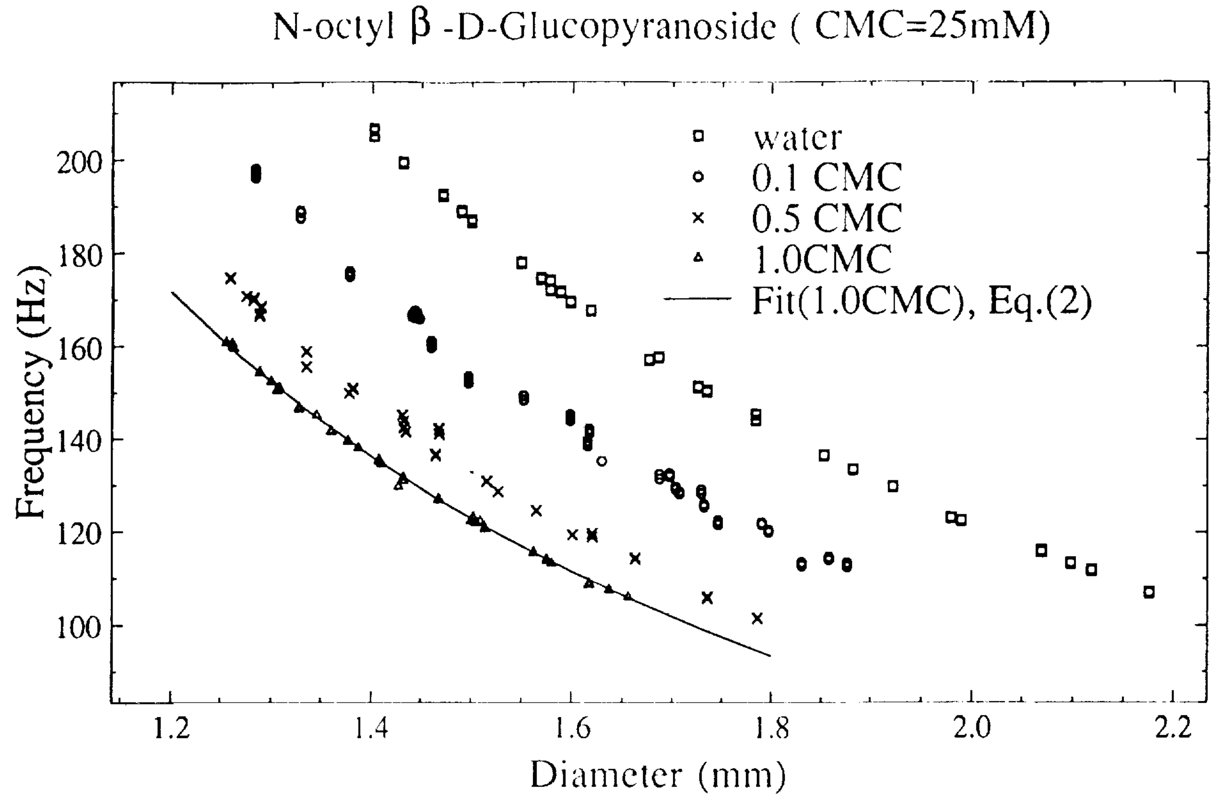


Figure 7 Experimental (ultrasonic) and theoretical results for the change in shape oscillation frequency with aspect ratio for the 1g case.



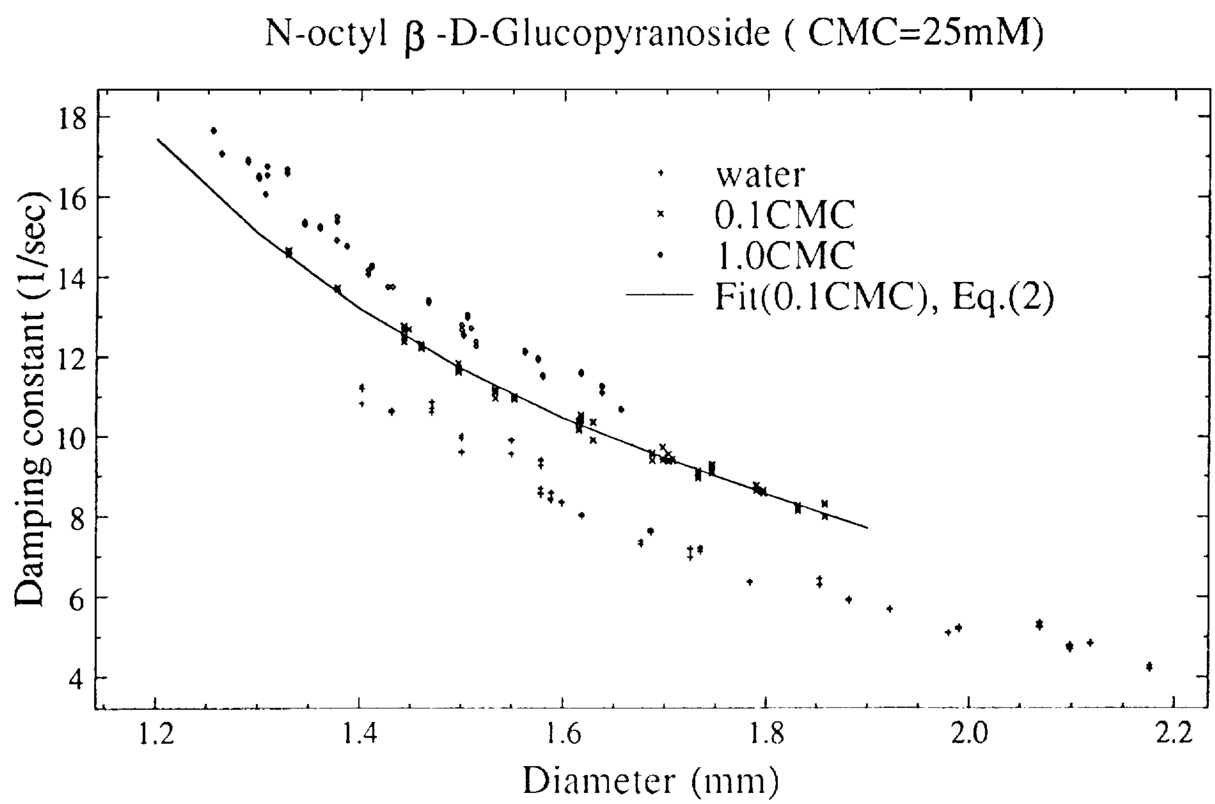


Figure 8 Measured free shape oscillation frequency and damping constant vs. drop diameter for water drops containing varying amounts of N-octyl b D-glucopyranoside, a nonionic surfactant. Measurements were at 1g.

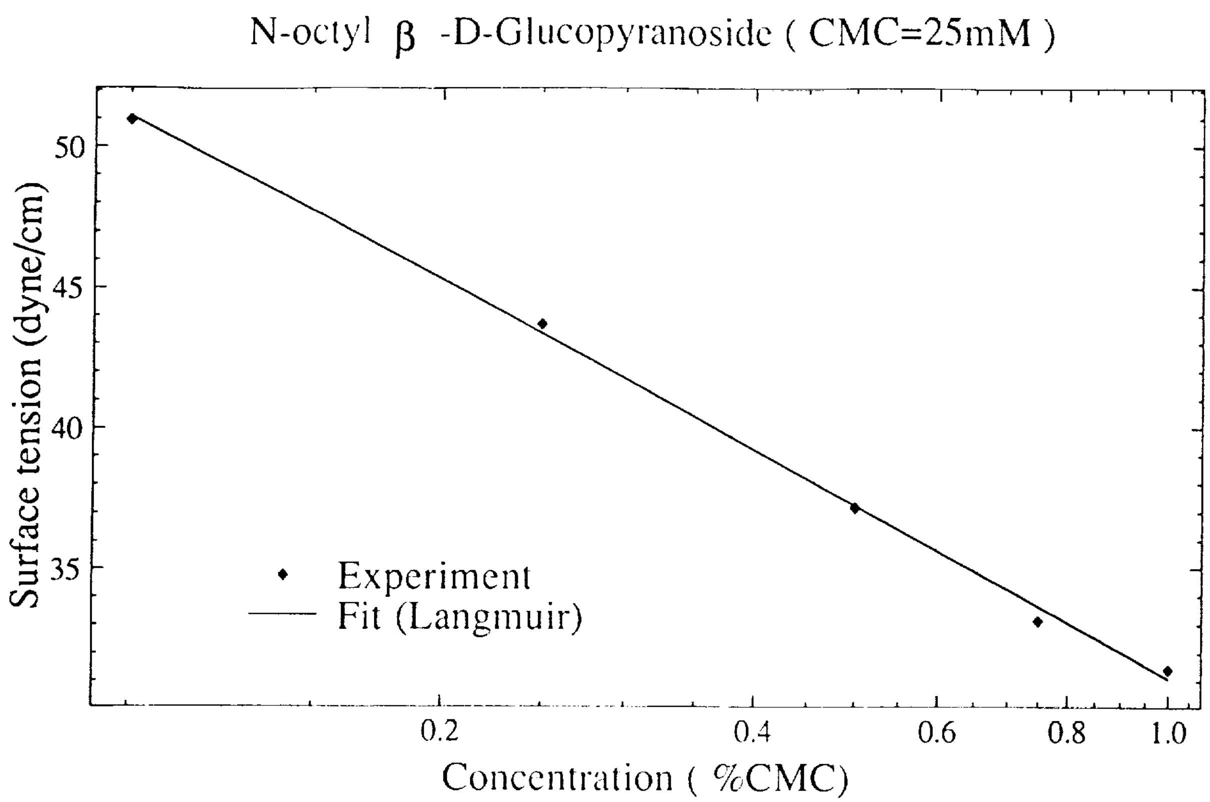


Figure 9 Surface tension vs surfactant concentration, based on theoretical model and experimental results as shown in figure 8.

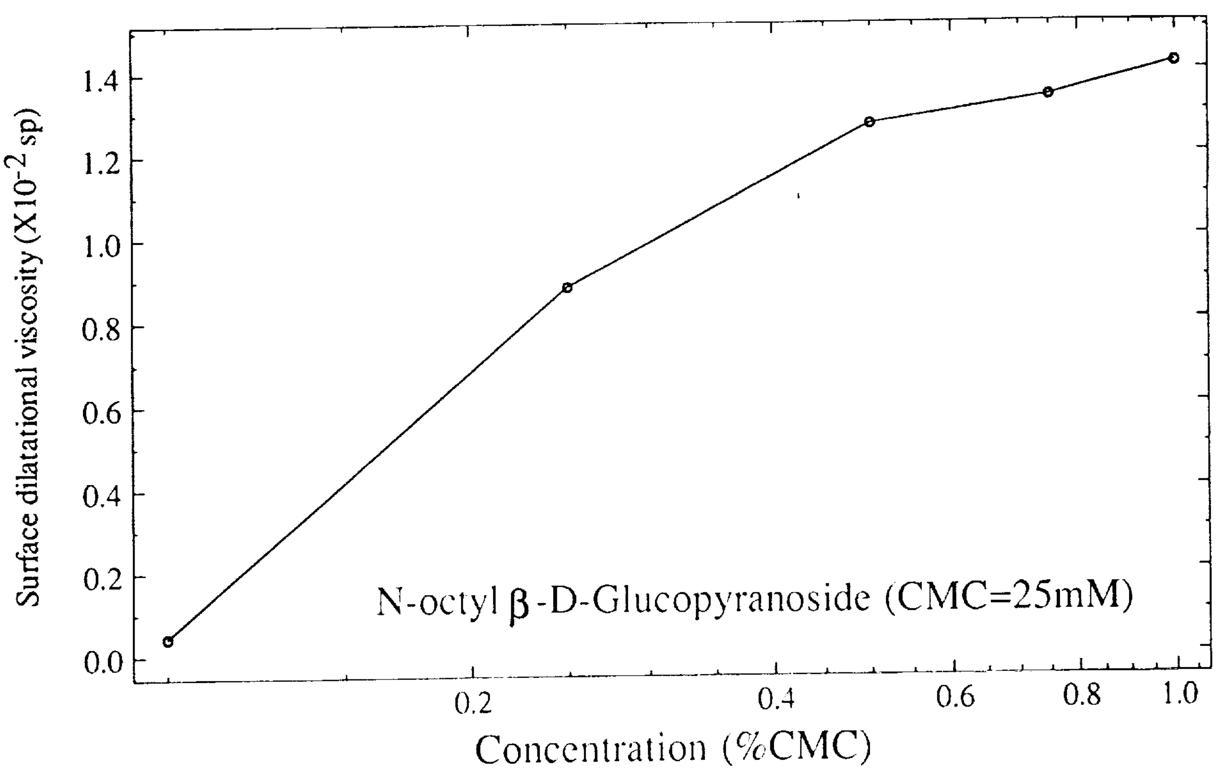


Figure 10 Surface dilatational viscosity vs. surfactant concentration, based on theoretical model and experimental results as shown in figure 8.

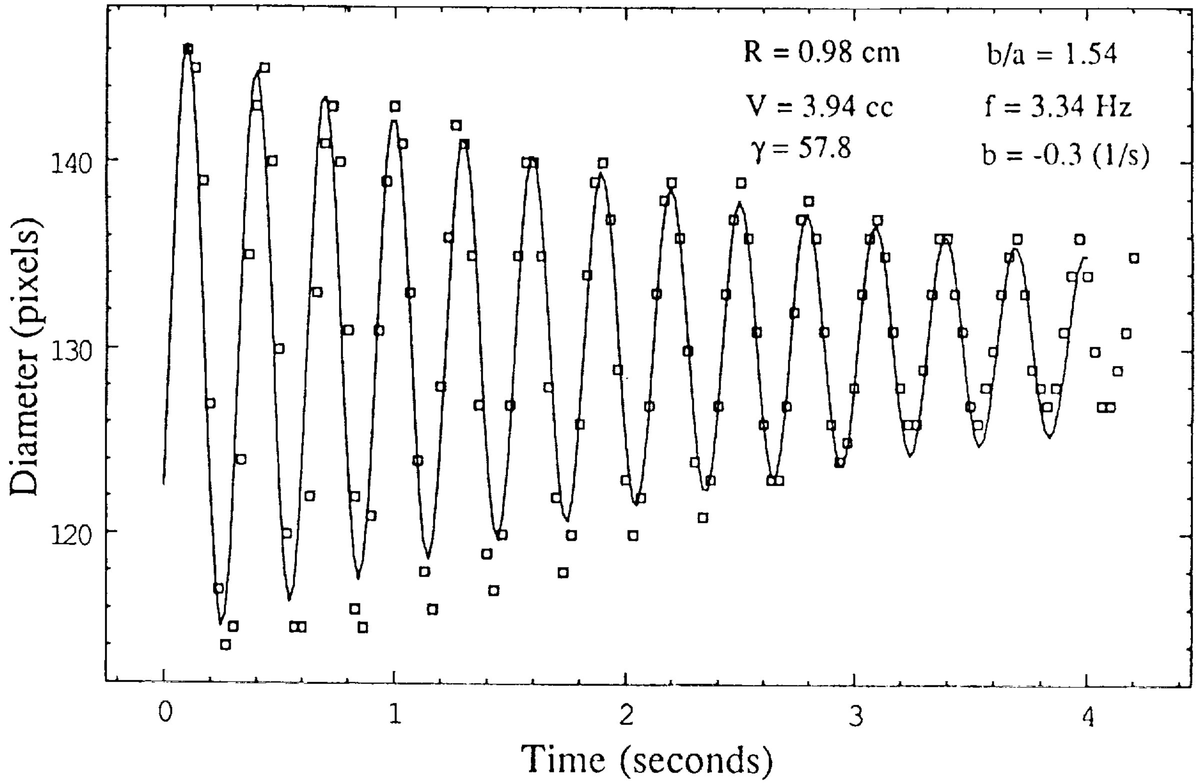


Figure 11 Microgravity data from video tape records for shape oscillations of a water drop.

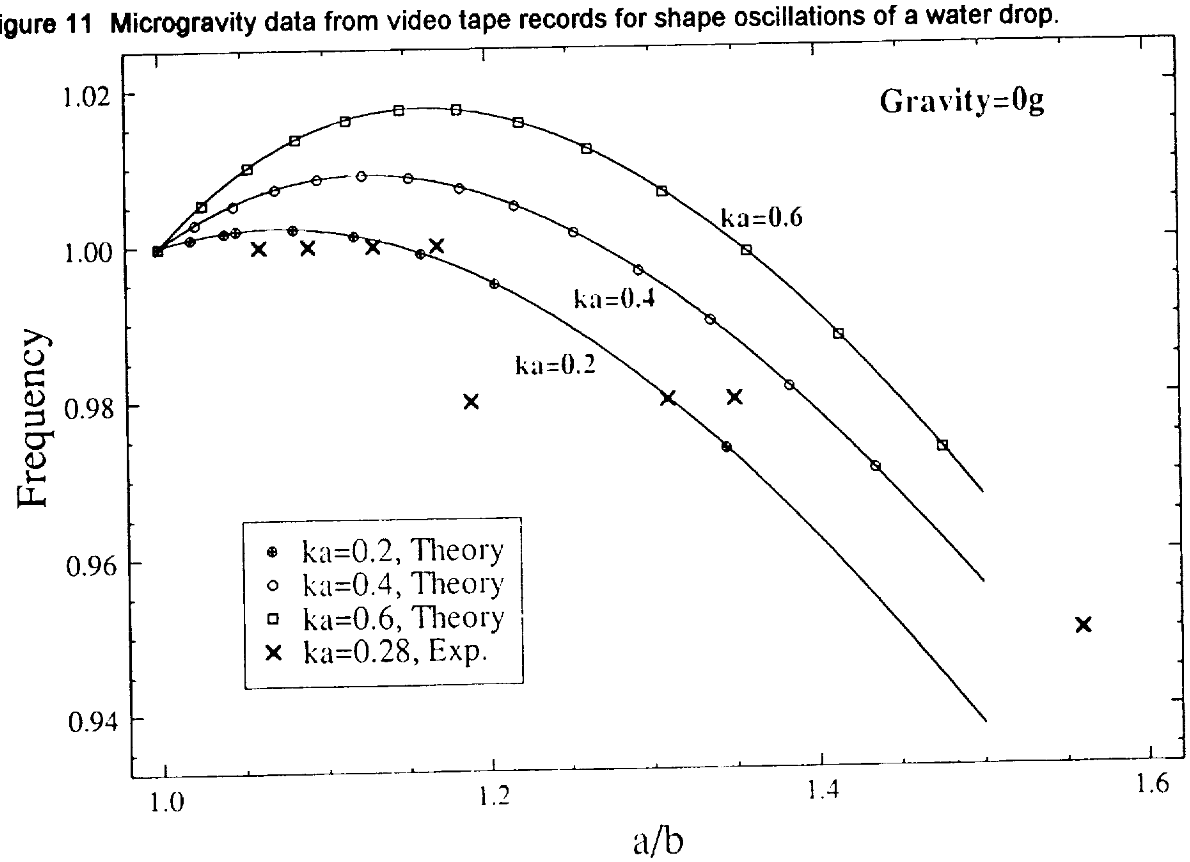


Figure 12 Spacelab experimental results from USML-1, based on data analysis of film, and theoretical predictions at 0g.

Discussion

Question: *In your slides, you had interaction between the bulk motion and the surface motion, however, you never included bulk viscosity in these. Can you explain that ?*

Answer: That is definitely in the equations.

Question: *But not in the slide ?*

Answer: I hate to disagree with you. This term is the viscosity in both fluids. There is an analysis presented in the written paper that will give those parameters and how they are interrelated. This is based on the work done by Lou that is recorded in the Journal of Fluid Mechanics for oil and water which we have changed, reduced, and simplified for the case of just a water drop surfactant in air, which makes the analysis much easier to deconvolve.

Comment : *Do I gather this correctly from your observations, that the drop dynamics with the usual Kelvin equilibrium equation does seem then to lead to satisfactory results in your opinion for all the observations ? Or are there some additional changes (involved) to that boundary condition, either to the dynamics of that absorption or whatever ? I gathered from your talk that you seemed quite satisfied.*

Answer: The Kelvin equation will do all right for the static case. But for the dynamic case, of course, you have to include these additional terms. We have a long way to go to be able to answer questions like you are asking.

Comment: *The reason I asked the question is that, I was very impressed with the damping data that you showed.*

Question: *However, the extraction of the properties from the damping data implicitly assumes that the Kelvin boundary condition is fine and then you get the result out, which is in accord with that assumption. I am wondering, that since the Kelvin equation is strictly an equilibrium statement, whether you are comfortable with proceeding from that point and extracting surface properties ?*

Answer: One thing we have to do, is we have to compare some of our results with some of the best data done by other methods. That's going to help us focus in on this question about whether the parameters we measure are unique or real material properties and that is an excellent question.

Question: *On your coalescence experiment, that looked far from random; Is that because of the acoustic field ?*

Answer: Yes. You saw when the drops get closer together there is actually a secondary force that pulls them to themselves, because they are both oscillating in the sound field and get about 1 diameter away. So that process is not random it's totally controlled by the acoustic field.

Question: *Could you comment on the error analysis on the second set of data ?*
Answer: Our error bars were quite large in this high aspect ratio because we are getting this tumbling rotation going on at the same time. I mean we have to do these experiments again. There is absolutely no question about the quality of the data is greatly compromised by tumble rotation and also with bubbles in the drops.

Comment: *So it is not due to your release mechanism. The reason I am asking is because you have different aspect ratios, so there has to be some variation in frequency despite all other factors.*
Answer: I think the error bars are large and it is not an uniform error bar. Part of the thing is just how you do the data analysis, how you get the frequencies from these plots. You do the Fourier transform of this thing. You try to get the frequencies but the data analysis is not adequate at this stage. I think, I wouldn't want to say that this is showing any real physical trend, I think it is more problem with the data quality.